

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to Cellulosic Sponge Material.

We, SPONCEL LIMITED, a British Company, DAVID THOMAS JONES, a British Subject, and FRANK BAYNHAM CROSS, a British Subject, all of 40 Chancery Lane, 5 London W.C.2, and W. & R. BALSTON LIMITED, a British Company of Springfield Mill, Maidstone, Kent, do hereby declare the invention, for which we pray that a 10 patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to cellulosic sponge materials, and more particularly to such 15 materials having groups attached to the cellulose structure which groups have inherently ion-exchange properties.

According to the present invention there 20 is provided a process for making a cellulosic sponge material which process comprises reacting hydroxyl groups of cellulosic sponge with a reagent such as to provide groups attached to the cellulosic structure, which groups have inherently ion-exchange 25 properties.

The reagent may, for example, contain 30 an oxyacid of phosphorus e.g. orthophosphoric acid and such a reagent will provide groups attached to the cellulose structure by reaction with the hydroxyl groups to provide a phosphorylated cellulose. The preparation of phosphorylated celluloses is known to those skilled in the art and can be achieved by a variety of methods.

35 For example, the phosphorylation of cellulose may be carried out by saturating cellulose with a reagent comprising urea and orthophosphoric acid, squeezing or otherwise removing most of the reagent and then 40 curing the treated cellulose in an oven at a temperature of about 130° C. for 2 to 3 hours or more. The concentration of the

reagent and the temperature and time of the curing stage will control the degree of phosphorylation. This technique of phosphorylation may be applied to regenerated cellulosic sponge in accordance with this invention. The treated sponge is washed to remove unreacted reagent and may be dried at 45 80° C to provide a regenerated cellulosic sponge having ion-exchange properties. A cellulosic sponge material may thus be prepared having an ion-exchange capacity of 0.5 to 5 or 10 meq/g.

The cellulosic sponge material in accordance with this invention may be in the form of blocks, or continuous sheets which may have a cotton scrim laminate. The regenerated cellulose may have a variety of fibres incorporated to provide reinforcement. Conveniently the regenerated cellulosic sponge may be in a cloth-like form prepared by rolling out a crystal paste of viscose and subsequently regenerating the cellulose in the manner known *per se*. Phosphorylation of such a sponge cloth material provides an ion-exchange material in a readily usable form. The novel ion-exchange material according to the invention may be employed, for example, for the extraction of catalyst from acid solution.

50 Alternative reagents which when reacted with hydroxyl groups of cellulosic sponge provide groups attached to the cellulose structure which have inherently ion-exchange properties are:—

(1) solutions of sodium chloroacetate and strong alkali which result in carboxymethyl groups being attached to the cellulose;

(2) solutions of citric acid which result in citrate groups being attached to the cellulose;

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- (3) solutions of aminoethylsulphuric acid and strong alkali which result in aminoethyl groups being attached to the cellulose;
- 5 (4) solutions of 2-chloro triethylamine hydrochloride and strong alkali which result in diethylaminoethyl groups being attached to the cellulose;
- (5) solutions of epichlorohydrin, triethanolamine and strong alkali which result in basic groups containing tertiary nitrogen being attached to the cellulose. Certain reagents will only react with the cellulosic sponge either after mercerisation of the latter, or without mercerisation but in the presence of strong alkali during the reaction stage. A strong alkali is one such as an alkali metal hydroxide.
- The invention also includes a cellulosic sponge material having groups attached to the cellulosic molecules which groups have inherently ion-exchange properties.
- Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE I.

A cellulose sponge material was prepared by reacting 65 parts by weight of aqueous alkali cellulose (approximately 26% cellulose, 15% NaOH) with 12.0 parts carbon disulphide to produce cellulose xanthate. Viscose was made from the xanthate by mixing with 120 parts of 12 g/litre NaOH solution and 8.5 parts flax or hemp fibre. To this viscose mix was added 1000 parts by weight of crystalline Glaubers salt ($\text{Na}_2\text{So}_4\text{JOH}_2\text{O}$). The resulting crystal paste was loaded into shaped moulds and coagulated in sodium sulphate solution containing from 200 to 700 g/litre of the dehydrate at a temperature of 95° to 100° C where the Glaubers salt was dissolved out and the cellulose regenerated in the form of a cellular mass. The cellulose sponge material was washed free of salt solution and dried at 75° C.

The cellulose sponge thus obtained was phosphorylated by treating it with a solution of 50% (W/W) urea and 18% (W/W) orthophosphoric acid and squeezing out the sponge to retain an amount of solution of approximately three times the weight of dry cellulose. The sponge was then cured in an oven at 130° C. for 4 hours, then washed free from treating solution before drying at 80° C. The resulting sponge material had an ion-exchange capacity, in respect of the strong acid group, of 2.60 meq/g. and was strong enough to handle. The total ion-exchange capacity was 5.20 meq/g.

EXAMPLE II.

Sponge cloth material was prepared by

rolling out the crystal paste as prepared in Example I into a thin cloth which was then regenerated with an acid/sodium sulphate solution between 5 and 15% W/V with respect to sulphuric acid and containing from 200 to 700 g/litre of sodium sulphate dehydrate at 75° to 85° C. The cloth was washed free from acid and salts before drying at 75° C.

The dried cloth was then treated with a 50% (W/W) urea/18% (W/W) orthophosphoric acid solution, squeezed out to retain an amount of solution of about 3 times the cellulose weight and cured at 130° C. for 3 hours. The cured sponge cloth was washed free of treating solution before drying at 80° C.

The cellulose sponge cloth material so produced had an ion-exchange capacity, in respect of the strong acid group, of 2.3 meq/g.; the total ion-exchange capacity was 4.6 meq/g.

The sponge cloth may be formed with or without reinforcement, for example, by incorporating in the regenerated cellulosic sponge a woven cotton cloth.

The cellulosic sponge material may be prepared by methods other than regenerating a crystal paste, such methods known to those skilled in this art include the formation of a cellulosic sponge material by heating cellulose in block form or by coagulating electrically a dispersion of cellulose.

Phosphorylated cellulosic sponge as made by the process described in Example II may be employed in a variety of shapes and sizes; the phosphorylated cellulosic sponge so produced may combine the practical advantage of a high ion-exchange capacity together with a good structural rigidity and high rates of flow of liquids through the sponge.

EXAMPLE III.

A piece of dried cellulose sponge cloth material with a woven cotton cloth reinforcement was treated with a solution consisting of 9% (W/W) 2-chloro-triethylamine hydrochloride and 4.5% (W/W) sodium hydroxide. The sponge was squeezed out to retain an amount of solution of approximately eight times the weight of dry cellulose, and was then cured in an oven at 85° C for 3½ hours. Finally, the sponge was washed free from excess reagents and dried at 60° C.

The resulting sponge cloth material was found to have anion exchange properties and exhibited an ion-exchange capacity of 0.57 meq/g.

EXAMPLE IV.

A piece of dry regenerated viscose sponge was steeped in a solution consisting of 10% (W/W) aminoethyl sulphuric acid (W/W) and 10%

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- (W/W) sodium hydroxide. The excess solution was removed by squeezing until the sponge cloth retained an amount of solution equivalent to eight times the weight of the sponge. The sponge cloth was then oven cured at 110° C. for 2½ hours. Finally, the product was washed and dried at 60° C.
- The cellulose sponge cloth material so produced had anion exchange properties and exhibited an ion-exchange capacity of 0.81 meq/g.
- EXAMPLE V.**
- A sponge was treated as described in Example IV above, except that the solution composition was 7.5% aminoethyl sulphuric acid (W/W) and 7.5% sodium hydroxide (W/W).
- The product had an ion-exchange capacity of 0.41 meq/g.
- EXAMPLE VI.**
- A piece of dried cellulose sponge cloth was impregnated with a solution of 6.6% (W/W) sodium chloracetate and 12% (W/W) sodium hydroxide. The uptake of solution was controlled by squeezing until the cloth retained an amount of solution of approximately twelve times the weight of the dry sponge. The material was then maintained at a temperature of 30° C. in an incubator for 16½ hours. The product was highly swollen in water and there was a slight break up of the sponge structure. However, washing with N/2 hydrochloric acid caused deswelling and no further break up of the structure occurred. After further acid washing the sponge was washed free of excess electrolyte and dried at 60° C.
- The resulting sponge cloth material had a cation exchange capacity of 0.60 meq/g.
- EXAMPLE VII.**
- The procedure of Example VI was followed except that the reagent solution composition was 6.6% (W/W) sodium chloracetate and 8% (W/W) sodium hydroxide, and the reaction time was 18 hours.
- No visible break up of the sponge structure of the product was observed and the product, after regenerating with N/2 HCl and washing free of excess electrolyte had an ion-exchange capacity of 0.45 meq/g.
- WHAT WE CLAIM IS:—**
1. A process for making a cellulosic sponge material which process comprises reacting hydroxyl groups of cellulosic sponge with a reagent such as to provide groups attached to the cellulosic structure which groups have inherently ion-exchange properties.
 2. A process as claimed in Claim 1 wherein the reagent comprises an oxyacid of phosphorus to provide a phosphorylated cellulosic sponge material.
 3. A process as claimed in Claim 2 wherein the oxyacid of phosphorus is orthophosphoric acid.
 4. A process as claimed in any one of the preceding claims wherein the reaction conditions are such as to provide a phosphorylated cellulosic sponge material having an ion-exchange capacity of 0.5 to 10 meq/g.
 5. A process as claimed in Claim 1 wherein the reagent comprises a solution of sodium chloracetate and strong alkali to provide a cellulosic sponge material having carboxymethyl groups attached to the cellulose.
 6. A process as claimed in Claim 1 wherein the reagent comprises a solution of citric acid to provide a cellulosic sponge material having citrate groups attached to the cellulose.
 7. A process as claimed in Claim 1 wherein the reagent comprises a solution of aminoethyl sulphuric acid and strong alkali to provide a cellulosic sponge material having amino ethyl groups attached to the cellulose.
 8. A process as claimed in Claim 1 wherein the reagent comprises a solution of 2-chlorotriethylamine hydrochloride and strong alkali to provide a cellulosic sponge material having diethyl aminoethyl groups attached to the cellulose.
 9. A process as claimed in Claim 1 wherein the reagent comprises a solution of epichlorhydrin, triethanolamine and strong alkali to provide a cellulosic sponge material having basic groups containing tertiary nitrogens attached to the cellulose.
 10. A process as claimed in any one of the preceding claims wherein the cellulosic sponge is one containing a scrim reinforcing material.
 11. A process as claimed in any one of the preceding claims wherein the cellulosic sponge contains reinforcement in fibrous form.
 12. A process as claimed in any one of the preceding claims wherein the cellulosic sponge is a regenerated cellulosic sponge in a cloth-like form prepared by rolling out a crystal paste of viscose and subsequently regenerating the cellulose in the manner known *per se*.
 13. A process for making a cellulosic sponge material substantially as hereinbefore described in any one of the examples.
 14. A cellulosic sponge material when made by the process claimed in any one of the preceding claims.
 15. A cellulosic sponge material as

claimed in claim 14 which is in block or sheet form.

16. A cellulosic sponge material having groups attached to the cellulosic molecules which groups have inherently ion-exchange properties.

BOULT, WADE & TENNANT,
111 & 112 Hatton Garden,
London, E.C.1,
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Agents for the Applicants.

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